

# Department of Pesticide Regulation

# Gray Davis Governor Winston H. Hickox Secretary, California Environmental Protection Agency

## MEMORANDUM

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**Environmental Monitoring Branch** 

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**Environmental Monitoring Branch** 

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SUBJECT: PRELIMINARY RESULTS OF PESTICIDE ANALYSIS AND ACUTE

TOXICITY TESTING OF MONTHLY SURFACE WATER MONITORING FOR THE RED IMPORTED FIRE ANT PROJECT IN ORANGE COUNTY,

SEPTEMBER 2001 (STUDY 183)

#### **SUMMARY**

During September 2001, monthly surface water samples were collected from five sites in Orange County, California. Water samples showed no detects of fenoxycarb, hydramethylnon, pyriproxyfen, chlorpyrifos, dimethoate, and methidathion. Bifenthrin was detected in two samples at 0.108 and 0.503 parts per billion (ppb) at the two nursery sites. Diazinon was detected in three samples ranging from 0.048 to 12.25 ppb at two urban and an integrated site. Malathion was detected at one nursery site. Water samples collected from a mitigation filter strip planted with *Canna* showed an 11% reduction of bifenthrin concentrations.

#### SCOPE OF THIS MEMORANDUM

This memorandum reports results of water sampling conducted by the Department of Pesticide Regulation (DPR), under interagency agreement with the California Department of Food and Agriculture (CDFA), for the Red Imported Fire Ant (RIFA) control project. Data included here are from the September 25, 2001 monthly monitoring, and encompass results from chemical analyses. This memorandum summarizes results for bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, and five organophosphorus insecticides: chlorpyrifos, diazinon, dimethoate, malathion, and methidathion. Only bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, and chlorpyrifos are used in the RIFA control program. The other four organophosphates are in our multiresidue analytical method and are included in this report to assist in the interpretation of the toxicity results. An in-depth interpretation of data is not included here, but will be provided in the final report when the 2001 pesticide use report becomes available.

Reports of the monthly surface water sampling events will continue through the conclusion of the study. This memo is the twenty-fourth in the monthly sampling series. You can request

previous sampling results memos by calling the number above or you may view or download them from DPR's website at <www.cdpr.ca.gov/docs/rifa>.

#### MATERIALS AND METHODS

## **Sample and Data Collection**

On September 25, 2001, surface water samples were collected at five sites, C, D, E, F, and G within the Orange County treatment area (Table 1 and Figure 1) including one rinse blank. Sample at site G was collected at the outflow of the vegetative filter strip (see mitigation sampling). No sample was collected at site H due to lack of water. This sampling event did not coincide with measurable rainfall.

Table 1. Sampling site descriptions in Orange County, California

Site #	Description	Coordinates
A	Bolsa Chica Channel at Westminster Ave.	N 33°45'35", W 118°02'36"
В	East Garden Grove Channel at Gothard St.	N 33°43'03", W 117°59'59"
C	Westcliff Park	N 33°37'24", W 117°54'02"
D	Bonita Creek at San Diego Creek	N 33°39'03", W 117°51'49"
E	San Diego Creek at Campus Dr.	N 33°39'18", W 117°50'44"
F	Hines at Weir	N 33°42'30", W 117°44'19"
G	El Modeno Gardens	N 33°42'43", W 117°44'16"
Н	Marshburn Slough at Irvine Blvd.	N 33°41'45", W 117°44'02"
I	San Juan Creek at Stonehill Dr.	N 33°28'31", W 117°40'43"
J	Arroyo Trabuco at Oso Parkway	N 33°35'06", W 117°38'09"

All water samples were collected at center channel using a 10-liter stainless steel bucket and divided into one-liter amber sample bottles using a Geotech® 10-port splitter. Samples designated for organophosphate chemical analysis were preserved by acidification with 3N hydrochloric acid to a pH between 3.0 and 3.5. Because diazinon rapidly degrades under acidic conditions, it was analyzed from a separate, un-acidified sample. Samples designated for toxicity testing were delivered to the testing laboratory within 36 hours of collection. All samples were stored on wet ice or in a 4°C refrigerator until transported to the appropriate laboratory for analysis.

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# **Mitigation Sampling**

In addition to the monthly surface water samples being collected at sites throughout Orange County, mitigation samples are being collected at El Modeno Gardens (site G) from a concrete lined ditch approximately 160 yards long, three and a half feet deep, and four to six feet wide. The filter strip consists of nine successive settling basins planted with *Canna x 'Tropicana'*. Water samples are collected at the inlet and outlet of the filter strip. At the time of this sampling *Canna* had been planted in all of the settling basins. Adding sandbags to increase the depth has raised the water level in the basins.

Water samples were collected and transported using the technique described previously.

#### **Environmental Measurements**

Water quality parameters measured *in situ* included temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO). Water pH was measured using an IQ Scientific Instruments® (model IQ 150) pH meter. EC, water temperature, and DO were measured using an YSI® multi parameter meter (model 85).

#### **Insecticide Analyses**

All water samples were analyzed for bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, chlorpyrifos, diazinon, dimethoate, malathion, and methidathion. The CDFA Center for Analytical Chemistry performed all analyses using gas chromatography and a flame photometric detector for the five organophosphorus insecticides; a high performance liquid chromatography and a ultra violet detector for fenoxycarb, hydramethylnon, and pyriproxyfen; and gas chromatography with an electron capture detector confirmed with a mass selective detector for bifenthrin. The reporting limit (reliable detection levels) for chlorpyrifos and diazinon is 0.04 ppb, 0.1 ppb for fenoxycarb and pyriproxyfen, 0.2 ppb for hydramethylnon, and 0.05 ppb for the other insecticides.

## **RESULTS and DISCUSSIONS**

#### **Insecticide Concentrations**

Of the nine insecticides analyzed, only chlorpyrifos, bifenthrin, fenoxycarb, hydramethylnon, and pyriproxyfen were allowed use in nurseries for treatment of fire ants to comply with the U.S. Department of Agriculture's quarantine requirements. All of the organophosphorus insecticides listed are registered for uses in commercial agriculture, nurseries, golf courses or parks for the control of other insect pests. Malathion and diazinon are widely available for homeowner use.

The Westcliff Park site, an urban drain, had the highest concentration of diazinon (12.25 ppb), with additional detections at Bonita and San Diego Creeks. Bifenthrin was only detected at the two nursery sites and did not contribute to residue in water at San Diego Creek.

The *Canna* vegetative filter strip showed an 11% reduction of bifenthrin residues. There were no reductions in malathion residues.

Table 2. Insecticide concentrations and acute toxicity in monthly surface water samples, September 2001, Orange County, California.

Concentration (ppb)									
Site	bifenthrin	fenoxycarb	hydramethylnon	pyriproxyfen	chlorpyrifos	diazinon	dimethoate	malathion	methidathion
С	$ND^1$	ND	ND	ND	ND	12.25	ND	ND	ND
D	ND	ND	ND	ND	ND	0.053	ND	ND	ND
E	ND	ND	ND	ND	ND	0.048	ND	ND	ND
F	0.108	ND	ND	ND	ND	ND	ND	ND	ND
G	0.503	ND	ND	ND	ND	ND	ND	0.134	ND
$RB^2$	ND	ND	ND	ND	ND	ND	ND	ND	ND

<sup>&</sup>lt;sup>1</sup> ND = none detected at the reporting limit for that chemical.

 $<sup>^{2}</sup>$  RB = rinse blank

Table 3. Insecticide concentrations at mitigation site, September 2001, Orange County, California.

Cumonia.									
	Conce	ntratio	n (ppb	)					
Location	bifenthrin	fenoxycarb	hydramethylnon	pyriproxyfen	chlorpyrifos	diazinon	dimethoate	malathion	methidathion
Surface Water Samples									
Filter strip inflow	0.563	$ND^1$	ND	ND	ND	ND	ND	0.108	ND
Filter strip outflow	0.503	ND	ND	ND	ND	ND	ND	0.134	ND

 $<sup>\</sup>frac{1}{1}$  ND = none detected at the reporting limit for that chemical.

# **Toxicity Data**

No toxicity samples were taken. The diazinon detection at site C was above the LC50's for both C. dubia and D. magna. Bifenthrin detections a sites F and G were above the  $LC_{50}$  for C. dubia. Table 4 gives LC<sub>50</sub> values for some aquatic organisms.

Table 4. LC <sub>50</sub> 's of insecticides (ppb) for three aquatic species. <sup>1</sup>					
Pesticide	Rainbow trout	D. magna	C. dubia		
Bifenthrin	0.15	1.6	$0.078^2$		
Chlorpyrifos	10	0.1	$0.13^{3}$		
Diazinon	3200	0.96	$0.51^4$		
Dimethoate	8500	2500	NA		
Fenoxycarb	1600	400	NA		
Hydramethylnon	160	1140	NA		
Malathion	68	1.0	$1.14^5$ - $2.12^6$		
Methidathion	10.5	7.2	2.2		
Pyriproxyfen	>325	400	NA		

<sup>&</sup>lt;sup>1</sup> Data from CDPR, 2000.

<sup>2</sup> Data from CDFG, 2000.

<sup>3</sup> Data from Menconi and Paul, 1994

<sup>4</sup> Data from Menconi and Cox, 1994

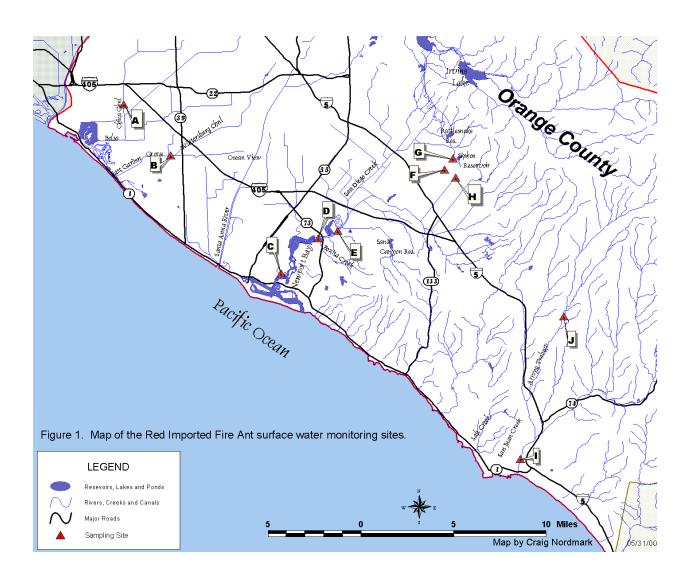
<sup>&</sup>lt;sup>5</sup>Data from Nelson and Roline, 1998 <sup>6</sup> Data from Ankley et al., 1991

#### **Environmental Measurements**

Table 5 presents the data for DO, temperature, pH, and EC. Ammonia, alkalinity, and hardness are only reported for site E since these measurements are taken with the toxicity tests. The California Regional Water Quality Control Board, Water Quality Control Plan, Santa Ana River Basin (1995), and the Water Quality Control Plan, San Diego Basin (1994), list the following water quality guidelines as acceptable: water temperature no higher than 78°F (25.5°C), pH between 6.5 and 8.5, and DO above 5.0 mg/L. The Santa Ana River Basin plan determines ammonia levels to be dependent upon water temperature and pH, while the San Diego Basin plan states that ammonia levels shall not exceed 0.025 mg/L. The plans do not provide an acceptable range for EC, alkalinity, or hardness. The temperatures at sites C, F, and G were above the maximum guideline.

Table 5. Water quality measurements at sampling sites, September 2001, Orange County, California.

Site	Temperature	рН	Dissolved Oxygen	Electroconductivity
	(°C)	•	(mg/L)	(µS/cm)
C	29.4	8.45	13.13	1328
D	19.9	7.12	8.15	3389
Е	24.7	7.1	9.47	3234
F	31.8	7.9	7.51	3066
G	25.6	6.64	2.93	2540
Filter strip inflow	28.5	7.67	9.74	2237
Filter strip outflow	25.6	6.64	2.93	2540



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#### References

Ankley, G.T., J.R. Dierkes, D.A. Jensen, and G.S Peterson. 1991. Piperonyl Butoxide as a Tool in Aquatic Toxicological Research with Organophosphate Insecticides. Ecotoxicology and Environmental Safety 21(3): 266-274.

CDFG. 2000. Pesticide Investigation Unit. Aquatic Toxicology Laboratory Report P-2161-2.

CDPR. 2000. CDPR Aquatic Toxicology Registration Database.

California Regional Water Quality Control Board. 1995. Water Quality Control Plan (Basin Plan), Region 8, Santa Ana River Basin. Riverside, California.

California Regional Water Quality Control Board. 1994. Water Quality Control Plan (Basin Plan), Region 9, San Diego Basin. San Diego, California.

Menconi, Mary, and Angela Paul. 1994. Hazard Assessment of the Insecticide Chlorpyrifos to Aquatic Organisms in the Sacramento-San Joaquin River System. California Department of Fish and Game, Environmental Services Division, Administrative Report 94-1.

Menconi, Mary, and Cara Cox. 1994. Hazard Assessment of the Insecticide Diazinon to Aquatic Organisms in the Sacramento-San Joaquin River System. California Department of Fish and Game, Environmental Services Division, Administrative Report 94-2.

Nelson, S.M. and R.A. Roline. 1998. Evaluation of the Sensitivity of Rapid Toxicity Tests Relative to Daphnid Acute Lethality Tests. Bulletin of Environmental Contamination and Toxicology 60: 292-299.

U.S. Environmental Protection Agency. 1993. Methods for measuring the acute toxicity of effluents and receiving waters to freshwater and marine organisms. 4th ed. EPA/600/4-90/027F. August 1993.

Precipitation data obtained from The University of California Statewide Integrated Pest Management Project, California Weather Databases. <www.ipm.ucdavis.edu/WEATHER/>